

Thermal Transitions and Extrusion of Glycerol-Plasticized Whey Protein Mixtures

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ABSTRACT: The effects of glycerol and moisture contents on the thermal transitions of whey protein isolate (WPI) powder–glycerol–water mixtures were studied. Mixtures with ratios of 100:0, 70:30, 60:40, and 50:50 WPI:glycerol on a dry basis (db) were preconditioned to 0.34 ± 0.01 (25.4 ± 0.4 °C) and 0.48 ± 0.02 (25.9 ± 2.2 °C) water activity. Differential scanning calorimetry (DSC) showed the existence of an endothermic peak starting at 148.3 ± 0.7 °C for 100% WPI preconditioned to a water activity of 0.34 ± 0.01 . The onset temperature of this peak decreased with addition and increase of glycerol content, as well as with the increase in water activity from 0.34 ± 0.01 to 0.48 ± 0.02 . An additional endothermic transition, important for extruding the mixtures into flexible sheets, occurred in mixtures containing 50% glycerol db, preconditioned to 0.48 ± 0.02 water activity. The onset temperature of the peak was 146 ± 2.0 °C. Whey protein-based sheets containing 45.8%, 48.8%, and 51.9% glycerol db were obtained using a Haake–Leistritz corotating twin-screw extruder. All samples were obtained at a screw speed of 250 rpm and a final barrel-temperature profile of 20, 20, 20, 80, 110, and 130 °C. Melt temperature at the time of sheet formation was 143 to 150 °C. Average thickness of the sheets was 1.31 ± 0.02 mm. Samples with 45.8% glycerol db had significantly higher tensile strength (TS) than samples with higher glycerol contents. Also, as glycerol concentration increased, sheet elastic modulus (EM) decreased significantly ($P \leq 0.05$). Extrusion of whey protein-based sheets is an important step toward extrusion of thinner edible films for food wraps, layers, or pouches.

Keywords: edible films, extrusion, tensile properties, thermal transitions, whey protein

Introduction

Increasing interest in high-quality food products with extended shelf life and reduced packaging waste has encouraged the study and development of edible and/or biodegradable polymer films and coatings (Krochta and De Mulder-Johnston 1997; Krochta 2002). Whey proteins can be formed into flexible, transparent films with excellent oxygen-, aroma-, and oil-barrier properties at low relative humidity. Research on plasticized whey protein-based edible films has focused on the formation, barrier, and mechanical properties of the films obtained by casting and drying aqueous whey protein–plasticizer solutions (Pérez-Gago and others 1999; Sothornvit and Krochta 2000a, 2000b, 2001; Ustunol and Mert 2004). However, while appropriate for studying the properties of films that would be formed as coatings on foods, the solution-casting method does not lend itself to large-scale production of films that could be used as stand-alone food wraps, or layers between food components, or sealed to form food pouches.

Whey protein-based films have also been successfully made from whey protein isolate (WPI) powder combined with either glycerol or water by thermal-compression molding (Sothornvit and others 2003). Such films were tested for film–water vapor permeability (WVP) and solubility to determine the effect of for-

mulation moisture and glycerol content. Manufacturing of batch compression-molded whey protein-based films constitutes the 1st step toward a more efficient, faster, and continuous extrusion process. Tubular or blown film extrusion and flat film or slit-die extrusion processes are widely used in the manufacture of synthetic plastic films. Calendering contributes to better thickness control. Calender rolls are widely used in the production of poly(vinyl chloride) sheet and film (Robertson 1993). Studies on extrusion of certain biopolymers such as starch, soy protein, and caseinate (Mungara and others 1998; De Graaf and Janssen 2000; Fossen 2000; Li and Lee 2000; Nabeshima and Grossman 2001) suggest the possibility of extruding whey proteins to form films.

Continuous extrusion of whey protein films would result in increased commercial potential and interest by the food and packaging industries. Mechanical properties of film, such as strength and flexibility, play an important role in the manufacturing and handling of stand-alone films that could further be sealed to form pouches for dry foods and ingredients.

It was hypothesized that the thermal transitions of different WPI powder–glycerol–water mixtures are related to the temperatures required for extrusion of WPI powder with varying glycerol contents into transparent, flexible sheets.

Therefore, the objectives of this study were to (1) determine the effects of glycerol content and moisture level on the thermal transitions of WPI powder–glycerol–water mixtures, and then (2) use the information on transition temperatures found in objective (1) to achieve the temperature profile needed to extrude the mixtures into sheets.

Extrusion of whey protein sheets constitutes the 1st step toward extrusion of thinner edible films, which can work together with conventional packaging to improve food quality while reducing nonbiodegradable solid waste.

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Materials and Methods

Thermal transitions

Materials. WPI powder (BiPRO) was obtained from Davisco Foods Intl. Inc. (Le Sueur, Minn., U.S.A.). The composition of the WPI powder was reported as 97.6% protein db, 2.1% ash, and 4.5% moisture. Glycerol was obtained from Starwest Botanicals Inc. (Rancho Cordova, Calif., U.S.A.). Saturated salt solutions of magnesium chloride ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$) and magnesium nitrate ($\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) (Fisher Scientific, Fair Lawn, N.J., U.S.A.) were used to precondition the samples to 0.34 ± 0.01 ($25.4 \pm 0.4^\circ\text{C}$) and 0.48 ± 0.02 ($25.9 \pm 2.2^\circ\text{C}$) water activity, respectively.

Mixture preparation. Mixtures of WPI powder and glycerol were prepared at room temperature (RT) of $23 \pm 2^\circ\text{C}$ and room relative humidity (RH) of $35 \pm 5\%$ by mixing both components using a mortar and pestle for 10 min.

Preconditioning. WPI-glycerol mixtures containing 30% glycerol were placed in a weighing dish and the mixtures were allowed to equilibrate overnight in a cabinet maintained at either 34% RH and $25.4 \pm 0.4^\circ\text{C}$ or 48% RH and $25.9 \pm 2.2^\circ\text{C}$. The resulting mixture was a hard, dry mass that was ground in a food chopper (KitchenAid Portable Appliances, St. Joseph, Mich., U.S.A.) and passed through a U.S.A. standard test sieve nr 14 (Gilson Co. Inc., Columbus, Ohio). Grinding was not possible for WPI-glycerol mixtures with 40% and 50% glycerol because they were quite soft.

The mixtures obtained were placed in differential scanning calorimetry (DSC) stainless steel pans, water activity-determination cups, and moisture-determination cups and were then stored in RH-controlled cabinets for a minimum of 40 h to ensure accurate equilibration between the relative humidity in the cabinet and the water activity of the samples.

Water activity determination. Water activity was measured using an AquaLab model CX-2 (Water Activity Measurement, Decagon Devices Inc., Pullman, Wash., U.S.A.). The instrument was allowed to warm up for 1 h and calibrated with saturated salt solutions of magnesium chloride and magnesium nitrate, as previously mentioned.

Moisture content determination. The vacuum oven moisture method (AOAC official method 927.05) for determination of moisture in dry milk (oven temperature: 100°C ; sample size: 1 to 1.5 g) was used to determine the moisture content of 100% WPI powder

and WPI-glycerol mixtures preconditioned to 0.34 ± 0.01 ($25.4 \pm 0.4^\circ\text{C}$) and 0.48 ± 0.02 ($25.9 \pm 2.2^\circ\text{C}$) water activity. A vacuum oven equipped with a moisture trap was used to pull a vacuum of 22 to 25 inches of mercury. After drying, the samples were sealed and equilibrated to room temperature inside a desiccator before weighing them. Since the weights of the 3 different samples remained constant after 23, 26, and 30 h of drying, subsequent measurements were taken only after 24 ± 3 h.

DSC characterization. A differential scanning calorimeter (DSC-7, Perkin Elmer, Norwalk, Conn., U.S.A.), a thermal analyzer controller (TAC 7, Perkin Elmer), and an intracooler (model FC-50-100-PE, Perkin Elmer) were used to determine the thermal transitions of WPI-glycerol mixtures. PYRIS software version 3.81 (Perkin Elmer) was used for data analysis. Large volume (0.075 cc) stainless steel pans sealed with O-rings were used to enhance observations of thermal transitions and suppress interfering effects of heat of water vaporization. During each run, the DSC cell was flushed with nitrogen at 20 mL/min to maintain an inert environment. The instrument was calibrated using pure indium (melting point 156.6°C) and pure ice (melting point 0°C). Temperature scans were performed at a rate of $20^\circ\text{C}/\text{min}$.

Extrusion

Materials. Instantized WPI powder possessing a larger particle size (more suitable for the gravimetric feeder) than WPI powder and a reported composition of $96.6 \pm 0.2\%$ protein db, $2.0 \pm 0.1\%$ ash, $1.35 \pm 0.2\%$ soy lecithin, and a measured moisture content of $6.48 \pm 0.1\%$ and water activity of 0.26 at 25°C , constituted the solid feed during the extrusion of whey protein sheets. A mixture of 70% glycerol and 30% water constituted the liquid feed in the extrusion process.

Extrusion conditions. Sheets were extruded using a corotating twin-screw extruder (Haake-Leistritz Micro-18, Sommerville, N.J., U.S.A.) with 6 independent electrically heated and air-cooled sections (Figure 1). The extruder was equipped with a slit die measuring 25.4 mm in width and 1 mm in height. Each section of the extruder had a length-to-diameter ratio of 5:1. The screw diameter was 18 mm.

The 1st, 2nd, and 3rd sections of the extruder barrel were kept at room temperature (20°C). The final barrel temperatures for

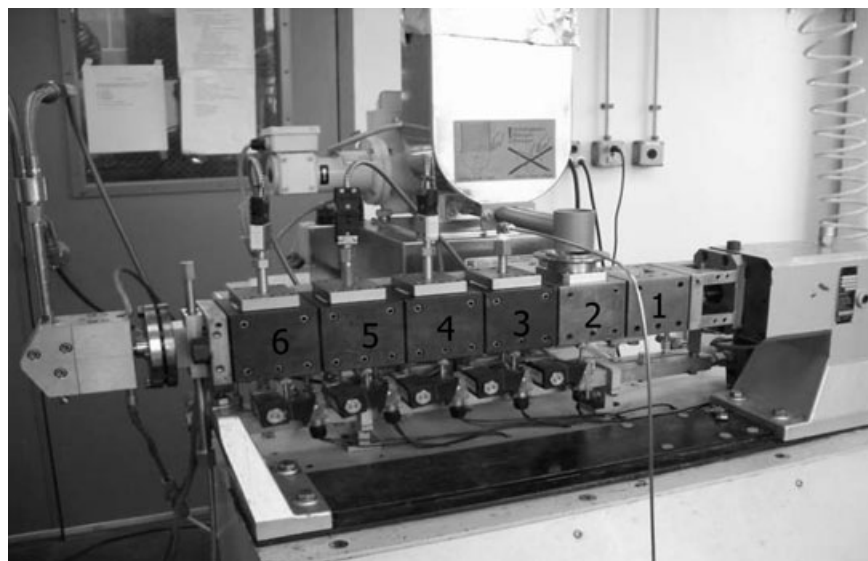


Figure 1 – Extruder barrel showing 6 independent electrically heated and air-cooled sections.

sections 4, 5, 6, and the die were set to 80, 110, 130, and 130 °C, respectively.

The screw configuration consisted of conveying elements of varying pitch (millimeters) and length (millimeters). Starting at the feed port, the dimensions, length [pitch], of the screw elements were 90[14], 60[14], 30[14], 30[10], 60[7], 60[5], 60[5], 20[5], 30[7], and 90[10].

Feed delivery into the extruder barrel. The solid feed (instantized WPI) was introduced into the 2nd section of the extruder barrel using a K-Tron gravimetric feeder (K-Tron America Inc., Pitman, N.J., U.S.A.) while the liquid feed (mixture of 30% water and 70% glycerol) was delivered into the 3rd section using a Bran+Luebbe metering pump (SPX Process Equipment, Delavan, Wis., U.S.A.). Flow rates during each extrusion run were monitored using a scale and a timer.

Color determination. Extruded sheets were preconditioned to a water activity of 0.5 ± 0.01 and a temperature of 25 ± 0.2 °C before color evaluation. A Minolta Chroma Meter (CR-200, Minolta Co. Ltd., Japan) calibrated with a white tile ($L^* = 94.4000$, $a^* = 0.3134$, $b^* = 0.3235$) was used to measure the color of the samples in the L^* , a^* , and b^* color notation system. Color measurements were conducted in triplicate by holding the measuring probe in direct contact with the extruded sheets against a white background.

Sheet thickness. Thickness of the extruded sheets preconditioned to a water activity of 0.5 ± 0.01 and a temperature of 25 ± 0.2 °C was determined using an electronic digital caliper model S 225 (Fred V. Fowler Co. Inc., Newton, Mass., U.S.A.). Thickness was measured at 5 random positions on the dog-bone shaped samples used for tensile testing.

Tensile properties. Tensile measurements of extruded sheets preconditioned to a water activity of 0.5 ± 0.01 and a temperature of 25 ± 0.2 °C were performed by pulling samples in the direction they exited the extruder. Measurements were made using an Instron universal testing machine Model 1122 (Instron Corp., Canton, Mass., U.S.A.) at a crosshead speed of 50 mm/min following the procedure outlined in ASTM method D882-97 (ASTM 1998). The testing environment was maintained at 50% RH and 23 ± 2 °C throughout the measurements. The tensile properties determined were: tensile strength (pulling force per initial sheet cross-sectional area at break, MPa), elastic modulus (sheet stiffness determined as the ratio of stress to strain in the linear region of the stress-strain curve, MPa), and elongation at break (degree to which the sheet can stretch before breaking, percent) (Krochta 2002).

Statistical analysis

Thermal transitions. A 2-factor completely randomized experimental design was used to study the effect of 4 levels of glycerol content (0%, 30%, 40%, and 50%) and 2 levels of water activity (0.34 ± 0.01 and 0.48 ± 0.02) on the thermal transitions of WPI-glycerol-water mixtures. All experiments were conducted in triplicate. The statistical computer program, SAS 9.1.3 (SAS Inst. Inc., Cary, N.C., U.S.A.), was used to perform analysis of variance (ANOVA) and multiple comparison (Fisher's LSD) tests. Significance was defined as $P \leq 0.05$.

Extrusion. A single-factor completely randomized experimental design was used to determine significant differences among the extruded samples. The factor studied was glycerol content of the extruded whey protein-based sheets at 3 levels (45.8%, 48.8%, and 51.9% glycerol db). The response variables were moisture content, color, thickness, and tensile properties of the extruded sheets. ANOVA and multiple comparison tests (Fisher's LSD) were used to determine the relationship between glycerol content and the properties of the sheets. All experiments were performed in triplicate. The statistical computer program SAS 9.1.3 was used to handle calculations.

Results and Discussion

Thermal transitions

Table 1 and 2 show that the moisture content of WPI-glycerol mixtures was affected not only by the water activity to which the samples were preconditioned but also by the glycerol content of the samples. The hydrophilic nature of glycerol resulted in higher moisture contents, which, in turn, contributed to a higher plasticization of the polymer matrix.

Samples heated from 0 to 250 °C at a rate of 20 °C/min (Figure 2c and 2d) showed the presence of multiple peaks starting at around 180 °C. These peaks were similar to those reported by Kim and Ustunol (2001) and can be attributed to degradation of multicomponent materials, where more thermally stable bonds would require higher energies to dissociate. To avoid degradation of the samples in the DSC, most replicates were scanned from 0 to 180 °C.

DSC showed the presence of an endothermic peak starting at 148.3 ± 0.7 °C for 100% WPI preconditioned to a water activity of 0.34 ± 0.01 . The onset temperature of this peak decreased with addition and increase of glycerol content (Figure 2) as well as with the increase in water activity from 0.34 ± 0.01 to 0.48 ± 0.02 .

Table 1 – Transition temperatures for whey protein isolate-glycerol mixtures preconditioned to a water activity of 0.34 ± 0.01 (25.4 ± 0.4 °C).

Formula WPI: glycerol	Moisture content (%)	Onset (°C)	Peak (°C)	End (°C)
100:0	7.30 ± 0.07^a	148.3 ± 0.7^a	162.3 ± 1.3^a	172.6 ± 2.3^a
70:30	12.08 ± 1.33^b	99.5 ± 0.5^b	109.3 ± 0.4^b	117.1 ± 0.6^b
60:40	12.10 ± 2.13^c	83.2 ± 1.2^c	97.6 ± 1.0^c	106.2 ± 1.2^c
50:50	15.64 ± 1.57^c	76.8 ± 0.5^d	89.5 ± 0.4^d	97.3 ± 0.3^d

Means followed by different letters in a column are significantly different ($P \leq 0.05$).
N = 3 for all treatments.

Table 2 – Transition temperatures for whey protein isolate-glycerol mixtures preconditioned to a water activity of 0.48 ± 0.02 (25.9 ± 2.2 °C).

Formula WPI: glycerol	Moisture content (%)	Onset (°C)	Peak (°C)	End (°C)
100:0	9.57 ± 0.05^a	133.0 ± 5.9^a	146.9 ± 5.6^a	156.9 ± 5.6^a
70:30	18.00 ± 0.53^b	95.5 ± 0.5^b	104.7 ± 0.5^b	111.4 ± 1.1^b
60:40	18.79 ± 1.66^{bc}	79.7 ± 0.3^c	89.0 ± 0.8^c	96.0 ± 1.2^c
50:50	21.77 ± 2.71^c	76.5 ± 0.6^c	86.4 ± 2.2^c	92.2 ± 2.7^c
		146.2 ± 2.0	164.7 ± 4.5	182.5 ± 7.3

Means followed by different letters in a column are significantly different ($P \leq 0.05$).
N = 3 for all treatments.

(Figure 3). An additional endothermic transition starting at 146.2 ± 2.0 °C was detected for samples containing 50% glycerol, preconditioned to 0.48 ± 0.02 water activity (Figure 3a). The occurrence of this endothermic transition was essential for the transformation of the mixtures into a thermoplastic-extrudable melt. Lower moisture and glycerol contents prevented detection of this endothermic

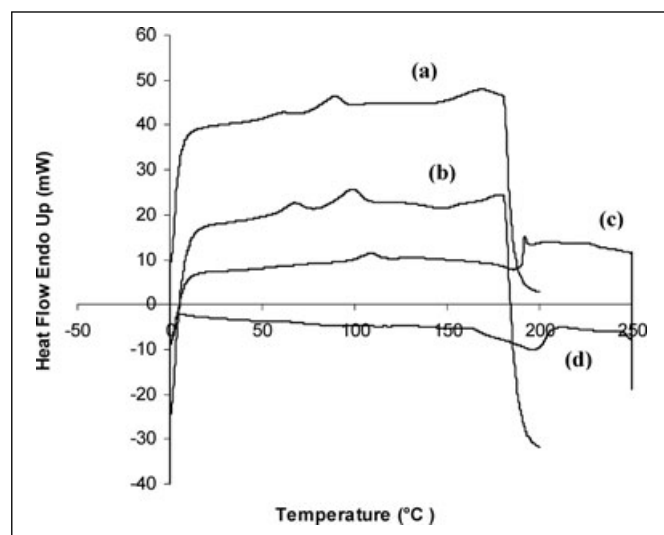


Figure 2—Differential scanning calorimetry thermogram of whey protein isolate (WPI):glycerol (gly) mixtures preconditioned to a water activity of 0.34 ± 0.01 (25.4 ± 0.4 °C). (a) 50:50 WPI:gly, (b) 60:40 WPI:gly, (c) 70:30 WPI:gly, and (d) 100:0 WPI:gly.

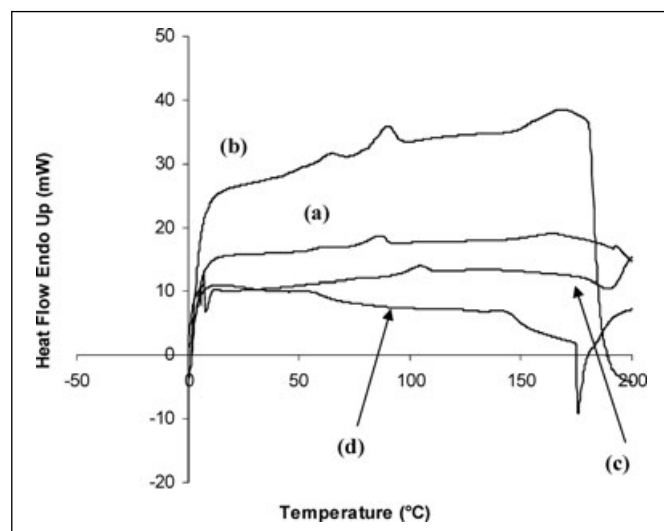


Figure 3—Differential scanning calorimetry thermogram of whey protein isolate (WPI):glycerol (gly) mixtures preconditioned to a water activity of 0.48 ± 0.02 (25.9 ± 2.2 °C). (a) 50:50 WPI:gly, (b) 60:40 WPI:gly, (c) 70:30 WPI:gly, and (d) 100:0 WPI:gly.

transition, and instead, multiple degradation peaks due to the rupture of chemical bonds occurred. DSC numerical data are reported in Table 1 and 2.

The 3 selected mixtures used for extrusion were 41:59, 44:56, and 47:53 solid:liquid ratio (Table 3). These mixtures were also characterized using DSC. In all 3 mixtures, the lower and higher endothermic transitions determined in 50:50 WPI:glycerol mixtures, preconditioned to 0.48 ± 0.02 water activity, were observed (Figure 4).

Extrusion

To facilitate the extrusion processing of the selected mixtures, an excess of liquid (solution of glycerol–water) was added. The amount of liquid was gradually decreased until continuous, flexible, transparent sheets started forming. This occurred at a composition of 51.9% glycerol db. Continuous sheets were also formed at 48.8% and 45.8% glycerol db (Table 3). Formation of uniform sheets continued at a lower limit of 42.8% glycerol db. Lower glycerol contents (samples with 40.9% glycerol db) produced highly discolored and consistently damaged (disrupted) sheets, probably due to high viscous heat dissipation and higher localized temperatures that resulted in product degradation. The melt temperature at the die for all 3 types of sheets was in the range of 143 to 150 °C. This range of temperatures can be related to the higher endothermic peak determined by DSC for mixtures containing 50% glycerol db preconditioned to a water activity of 0.48 ± 0.02 . The product-melt temperatures along the extruder barrel were recorded by thermocouples that were in direct contact with the product as it was being extruded. For sections other than the die, product temperatures were close to the barrel set temperatures. However, higher melt temperatures compared to set temperatures occurred in the die due to lack of air cooling in this section along with viscous heat dissipation and mechanical energy input, resulting in melt temperatures of 143 to 150 °C.

Continuous sheets did not form under 143 °C. Above a melt temperature of 153 °C, expansion (bubbles) in the sheets occurred, likely due to excessive evaporation of water from the sheets at this temperature.

Moisture content

Table 4 shows the average moisture contents of the extruded sheets equilibrated to a water activity of 0.5 and 24.9 ± 0.4 °C. ANOVA indicated that the average moisture contents of sheets containing 45.8%, 48.8%, and 51.9% glycerol db were not significantly different ($P > 0.05$) from each other.

Color

The b^* value provided the most useful information since it corresponds to the yellow (b^+)–blue (b^-) axis in the color scale and the color of the samples was mainly affected along this axis. Figure 5 shows the b^* values for samples containing different glycerol contents. ANOVA and Fisher's LSD tests indicated that samples with 45.8% glycerol db had a significantly higher ($P \leq 0.05$) b^* value than samples with higher glycerol contents. Higher discoloration was

Table 3—Conditions used to extrude whey protein-based sheets.

Total feed rate (g/min)	Solid ^a (%)	Liquid ^b (%)	WPI powder (db) (%)	Feed glycerol content (%)	Feed moisture content (%)	Percentage glycerol db in extruded sheet
18.2	47	53	44.0	37.1	18.9	45.8
18.2	44	56	41.1	39.2	19.7	48.8
18.2	41	59	38.3	41.3	20.4	51.9

^aInstantized whey protein isolate (WPI) powder with 6.48% moisture content.

^b70% glycerol, 30% water.

observed in preliminary experiments as glycerol content was decreased below 45.8%. This color change was accompanied by sheet damage due to viscous heat dissipation and higher localized temperatures, as mentioned previously in the extrusion section. Therefore, color changes might be an indication of protein degradation.

Table 4—Moisture contents of extruded sheets equilibrated to a water activity of 0.5 at 24.9 ± 0.4 °C.

Sample (%glycerol db)	Moisture content (%)
45.8	25.95 ± 2.62^a
48.8	24.15 ± 5.19^a
51.9	28.00 ± 3.18^a

Means followed by a superscript letter in a column are significantly different ($P \leq 0.05$).
N = 3 for all treatments.

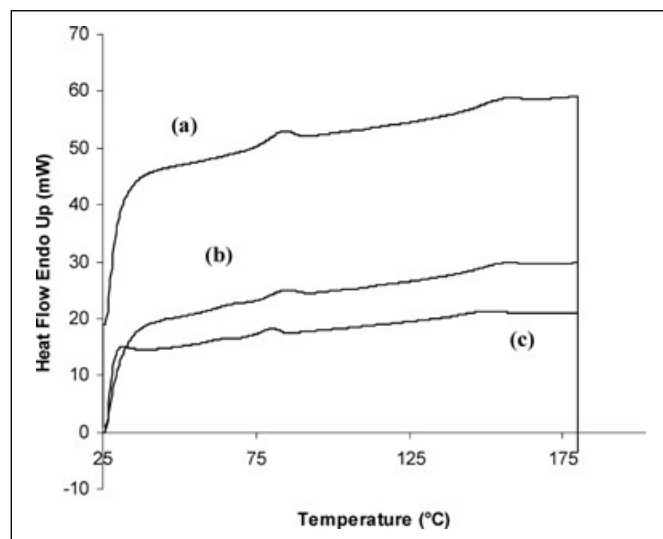


Figure 4—Differential scanning calorimetry thermogram of whey protein isolate (WPI)-glycerol (gly)-water mixtures used to extrude whey protein-based sheets. (a) 47:53 WPI:liquid*, (b) 44:56 WPI:liquid*, and (c) 41:59 WPI:liquid*. *Liquid consisted of 70% glycerol and 30% water.

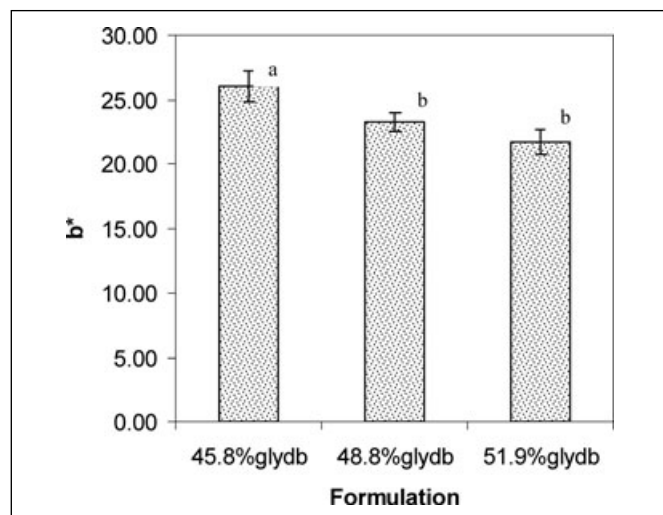


Figure 5—The b^* value of whey protein sheets with different glycerol contents. *Different letters above columns indicate significant differences.

Thickness

Some expansion occurred as sheets exited the die, resulting in greater sheet thickness and sheet width than the die thickness and die width.

The average thickness of the sheets was 1.31 ± 0.02 mm. ANOVA indicated that the thickness of the sheets was not significantly ($P > 0.05$) affected by their glycerol content.

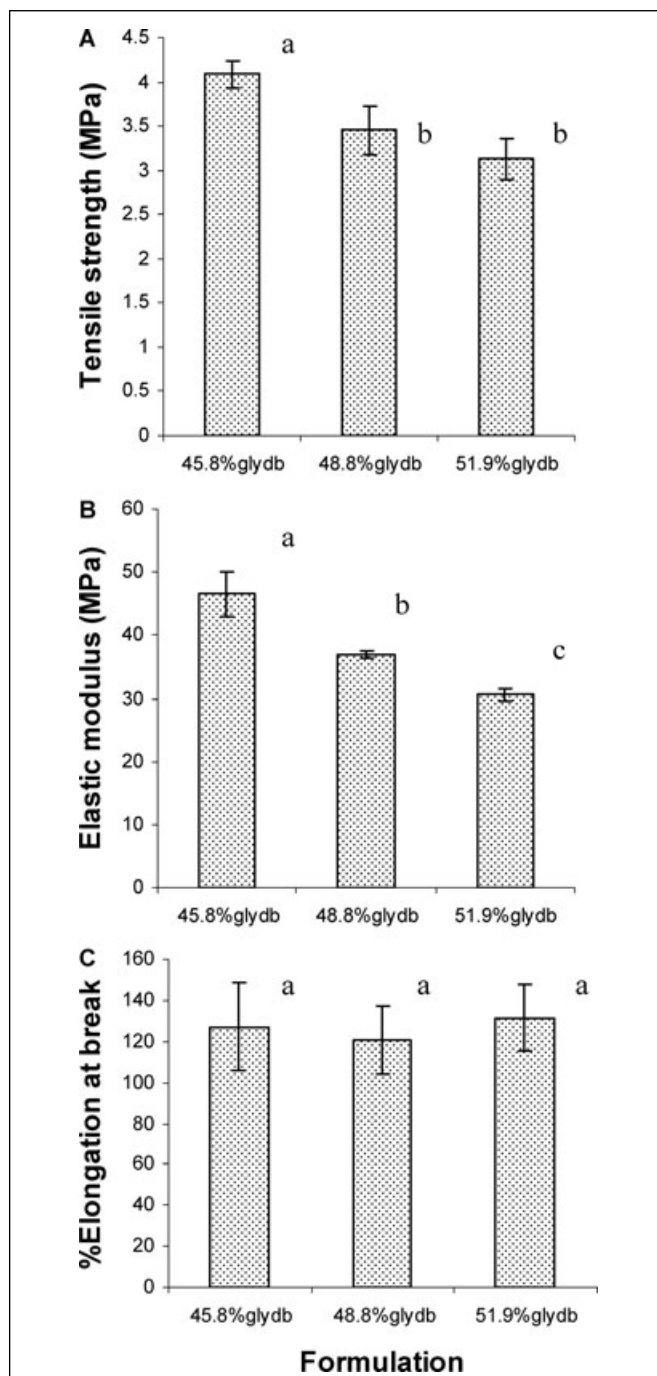


Figure 6—Tensile strength (A), elastic modulus (B), and percent elongation at break (C) of whey protein sheets with 45.8, 48.8, and 51.9% gly db. *Different letters above columns indicate significant differences.

Table 5—Comparison of the tensile properties of whey protein films and sheets obtained by solution casting, compression molding, and extrusion.

Method	Glycerol (%)	Tensile strength (MPa)	Elastic modulus (MPa)	Elongation (%)
Compression molding ^a	40	8	144	85
Compression molding ^a	50	4	60	94
Solution casting ^b	40	4.7	N/A	114
Solution casting ^c	45	3	106	45
Solution casting ^c	55	1.4	26	68
Extrusion	45.8	4.1	46.5	127
Extrusion	48.8	3.5	36.9	121
Extrusion	51.9	3.1	30.6	132

^aSothornvit and others (2007).^bUstunol and Mert (2004).^cSothornvit and Krochta (2000a).

For food applications, sheet thickness would have to be reduced about 1 order of magnitude. Reduced sheet thickness could be achieved using a die with a narrower slit. Alternatively, as the sheet comes out of the die, the sheet could be stretched by calender rollers to reduce sheet thickness. Another approach is the blown film process, which uses a circular die, with stretching of the extruded cylinder to a larger diameter by blowing air through the circular die as the melt exits the extruder.

Tensile properties

Although plasticizers such as water and glycerol are necessary to improve processability of the biopolymer matrix and overcome film brittleness due to protein–protein interactions, the amount of plasticizers added will greatly affect the mechanical properties of the resulting structures. In the present study, no significant differences were found in moisture contents among the extruded sheets with different glycerol contents (Table 4). Therefore, the differences in mechanical properties can be attributed to differences in glycerol contents.

Figure 6A to 6C illustrate the results obtained for the tensile strength (MPa), elastic modulus (MPa), and elongation at break (percent) of the extruded sheets with different glycerol contents. Samples with 45.8% glycerol db had a significantly higher ($P \leq 0.05$) tensile strength (TS) than samples with higher glycerol contents (see Table 5). As glycerol concentration increased, sheet elastic modulus (EM) decreased significantly ($P \leq 0.05$) from 46.5 to 30.6 MPa, resulting in a more flexible structure. The highest variability occurred for percent elongation at break (%E), where no significant differences ($P > 0.05$) were found among the samples. Compared to extruded synthetic polymer films such as low-density polyethylene, high-density polyethylene, and oriented polypropylene (Krochta 2002), extruded whey protein-based sheets had lower TS and %E values. Film toughness is also higher in conventional synthetic films, since it is calculated as the product of TS and %E. However, the application of edible films in food systems is generally such that the mechanical properties currently achieved are sufficient to obtain a high-quality food product (Krochta 2002).

Tensile properties for solution-cast and compression-molded whey protein films and sheets with varying glycerol contents have been reported (Sothornvit and Krochta 2000a; Ustunol and Mert 2004; Sothornvit and others 2007). Table 5 shows a comparison of the tensile properties of whey protein films and sheets with similar glycerol contents obtained by solution casting, compression molding, and extrusion. Samples made by extrusion had tensile properties similar to samples made by compression molding. Samples made by extrusion or compression molding had higher TS than samples made by solution casting. This can be attributed to a higher degree of cross-linking due to the applied heat and pressure in these 2 methods. EM was greatly affected by the plasticizer

content, as can be seen in solution-cast films with 45% and 50% glycerol content or compression-molded films with 40% and 50% glycerol. Percent elongation at break was higher for samples made by extrusion, probably due to a greater alignment of the polymer molecules in the machine direction as the sheets come out of the extruder die.

Conclusions

Material characterization by DSC constitutes a useful tool in understanding the role of glycerol and water during extrusion of whey protein-based sheets. Extrusion is a process in which temperature and mechanical energy contribute to a more extensive protein denaturation and cross-linking when compared to solution casting. Therefore, higher amounts of plasticizer and moisture are required to allow the thermal transitions to take place. Otherwise, degradation of the materials might occur before the desired product can be obtained. The higher endothermic transition detected by DSC (onset temperature of $146.2 \pm 2^\circ\text{C}$) was closely related to the melt temperature range (143 to 150°C) needed for extrusion of whey protein-based sheets. The occurrence of this transition appears to be essential to convert a mixture of whey protein isolate powder, water, and glycerol into a thermoplastic-extrudable melt. However, extrusion is a continuous process where the material is subjected not only to heating conditions but also shearing, mixing, and shaping under pressure. Therefore, information obtained from DSC analysis needs to be combined with an understanding of the effects of other extrusion conditions such as extruder dimensions, screw configuration, screw speed, heating/cooling capabilities, and feed rates for optimum extrusion of plasticized whey protein sheets.

Acknowledgments

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